POLYCHLORINATED ALKANES IN ARCTIC AIR

Anders R. Borgen, Martin Schlabach and Hans Gundersen

Norwegian Institute for Air Research, Instituttveien 18, P.O. Box 100, N-2027 Kjeller, Norway

Introduction

Polychlorinated alkanes (PCA), or chlorinated paraffins, are straight chained alkanes with varying degrees of chlorination. The industrial production of PCAs have been going on since the 1930's, and their use in the western world in 1977 was estimated to 230 ktons[1]. PCAs are mainly produced by direct chlorination of a petroleum fraction with molecular chlorine in the presence of UV-light[2].

PCAs have been used as high temperature and pressure lubricants as well as secondary plasticizers and flame retardants in plastics and paints[1,4].

Based on their chainlength, PCAs are divided into the categories: short chained (C_{10}-C_{13}), medium chained (C_{14}-C_{17}) and long chained (C_{18}-C_{30}), and further by their degree of chlorination, low (<50%) and high (>50%)[4]. With their relatively high assimilation and accumulation potential, the short chained and highly chlorinated PCAs have been paid most attention to. Although PCAs generally have shown low toxicity to mammals, the short chained PCAs have a carcinogenic potential in rats and mice[5]. They have also shown to be toxic towards certain species in the aquatic environment[4, 6-7], although at concentration levels several orders of magnitude higher than for TCDD[7].

The complexity of PCAs makes it difficult to provide an analytical method for their precise and specific quantitative determination. Due to the large number of isomers, complete chromatographic separation seems impossible at this point. Therefore several different approaches have been applied for quantifying PCAs as correctly as possible[1-3, 5, 8-10].

The aim of this study was to determine whether long range transport of PCAs in air can be regarded as a threat to the Norwegian Arctic environment.

Experimental

Air samples were collected at Mt. Zeppelin, Svalbard, in the period March to May 1999, using one glass fibre filter (GFF, Gelman type AE, No. 61635, >99% cut-off for 0,2 μm) and two PUF plugs (100 mm diameter, 50 mm thickness and density of 25 kg/m^3) fitted in a high volume air sampler. The sample size varied from 1700 to 2850 m^3. For each sample, plugs and filter were Soxhlet extracted for 8 hours with 300 mL n-hexane:diethyl ether (9:1). The extracts were concentrated to 0.5 mL and then fractionated on activated silica[11]. The fraction containing the PCAs were reduced to 100 μL. A 10 μL aliquot of each cleaned up extract was

added 10 µL of a secondary standard (a mixture of ^{13}C-labelled PCDD/Fs, and PCBs) and then homogenized in an ultrasonic bath prior to GC-MS analysis.

An HP5890 GC coupled to a VG AutoSpec, high resolution mass spectrometer, was used in ECNI mode with methane at a pressure of 2×10^{-5} mbar as reagent gas. The GC was operated in constant flow mode, 1 mL/min, with a temperature program starting at 90°C, then ramping to 150°C by 25°C/min and further to 300°C by 15°C/min, holding that temperature for 5 min. The injector temperature was 260°C. Due to software limitations each analysis was performed with three injections to cover the mass range of interest. The rest of each analysis and the quantifications were performed according to the method described by Tomy et al.[2], with minor modifications

Results and Discussion

The results are reported as the sum of C_{10}–C_{13} PCAs with 5-10 Chlorine substitutions, in pg/m^3. In addition the total sample amount for each sample, in ng, is also reported to be able to compare the sample values with the blank values. The results are shown in table 1.

Table 1. Concentrations of short chained and highly chlorinated PCAs in air at Mt. Zeppelin, Svalbard.

	Σ PCA (pg/m^3)	Σ PCA (ng)	M (av), (g/mole)
March 26th	9.0	24	394.0
April 9th	23	67	411.1
April 16th	28	49	403.0
April 30th	16	48	414.4
May 7th	57	97	409.3
Fieldblank Zeppelin		40	438.0
Lab. blank		7.7	415.4
Solvent blank		4.1	419.9
Standard 55,5% Cl		-	410.2

Some of the PCA formula groups have probably been underestimated due to phthalates and other electron capturing compounds still apparent in the cleaned up extract. It is likely that these compounds compete with the PCAs regarding the capturing of electrons, and in addition they may also cause other problems related to the performance of the ion source. An underestimation of some of the formula groups will also affect the Σ PCA and therefore more work is needed in the cleanup procedure of air samples to handle these problems.

The blank problem needs to be investigated more thoroughly as the blank values found were of the same order of magnitude as the samples. A further development of the sampling equipment together with an increase in the sample amounts are the first steps toward more reliable results. However it is likely that PCAs are apparent in the air at Mt. Zeppelin. Generally, the formula groups at concentration levels significantly above the blank value, are the more volatile formula groups (figure 1 and 2), and as a consequence the calculated average molar masses for the samples are lower than for the fieldblank, suggesting transport of PCAs by air.

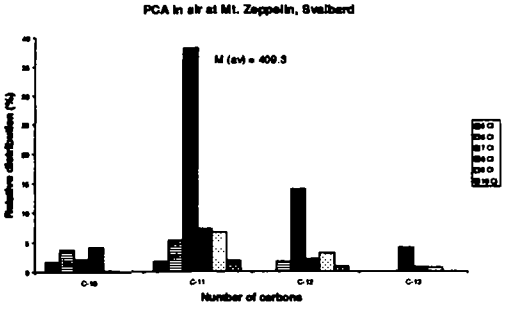

Figure 1. The relative distribution of the PCA formula groups in a selected sample from Mt. Zeppelin, Svalbard.

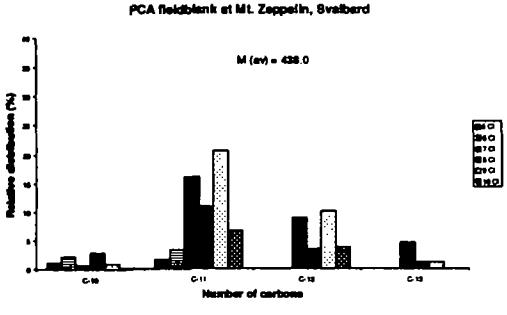

Figure 2. The relative distribution of the PCA formula groups in a field blank sample from Mt. Zeppelin, Svalbard

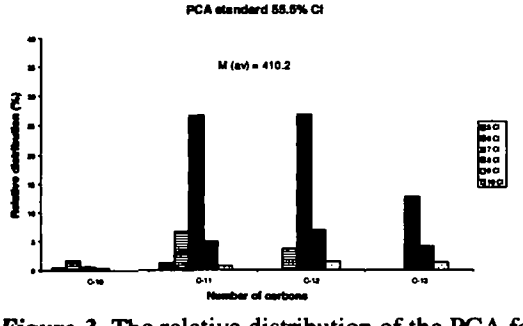

Figure 3. The relative distribution of the PCA formula groups in a standard containing a C_{10}-C_{13} mixture with 55,5 % Chlorine.

Acknowledgement

Anders R. Borgen would like to thank Gregg T. Tomy and Gary A. Stern at Freshwater Institute, Department of Fisheries and Oceans, Winnipeg, Canada, for their hospitality and generousity during his stay there in november 1999.
He would also like to thank The Research Council of Norway for financing this project.

References

[1] W. Kraemer and K.Ballschmiter, *Fresenius Z Analytical Chemistry (1987) 327:47-48*, Detection of a new class of organochlorine compounds in the marine environment: the polychlorinated paraffins.
[2] Gregg T.Tomy, *Thesis*, The mass Spectrometric Characterization of Polychlorinated n-Alkanes and the Methodology for their Analysis in the Environment.
[3]Nina Gjøs and Kay O. Gustavsen, *Analytical Chemistry 1982, 54, 1316-1318*, Determination of Chlorinated Paraffins by Negative Ion Chemical Ionization Mass Spectrometry.
[4] International programme on chemical safety, Environmental health criteria 181, Chlorinated paraffins
[5] Roland Rieger, Karlheinz Ballschmiter, *Fresenius' J. of Analytical Chemistry (1995) 352:715-724*, Semivolatile organic compounds-polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF), biphenyls (PCB), hexachlorobenzene (HCB), 4,4'-DDE and chlorinated paraffins (CP) as markers in sewer films.
[6] Mehmet Coelhan, Majlinda Saraci, Harun Parlar, *Chemosphere 40 (2000) 685-689*, A comparative study of polychlorinated alkanes as standards for the determination of C10-C13 polychlorinated paraffins in fish samples.
[7] Aaron T. Fisk, Gregg T. Tomy and Derek C.G. Muir, *Environmental Toxicology and Chemistry. Vol. 18. No. 12. pp. 2894-2902, 1999*, Toxicity of C_{10}-, C_{11}-, C_{12}- and C_{14}-polychlorinated alkanes to japanese Medaka (*Oryzias Latipes*) embryos.
[8] Bo Jansson, Renate Andersson, Lillemor Asplund, Åke Bergman, Kerstin Litzén, Kerstin Nylund, Lars Reuthergårdh, Ulla Sellström, Ulla-Britt Uvemo, Cajsa Wahlberg and Ulla Wideqvist, *Fresenius' Journal of Analytical Chemistry (1991) 340:439-445*, Multiresidue method for the gas-chromatographic analysis of some polychlorinated and polybrominated pollutants in biological samples
[9] S.A. Junk and H.-U. Meisch, *Fresenius' Journal of Analytical Chemistry (1993) 347:361-364*, Determination of chlorinated paraffins by GC-MS.
[10] Mehmet Coelhan, *Analytical Chemistry 1999, 71, 4498-4505*, Determination of Short-Chain Polychlorinated Paraffins in Fish Samples by Short-Column GC/ECNI-MS.
[11] Roland Kallenborn, Robert Gatermann, Sissel Planting, Gerhard G. Rimkus, Margrete Lund, Martin Schlabach and Ivan C. Burkow, *Journal of Chromatography A, 846 (1999), 295-306*, Gas chromatographic determination of synthetic musk compounds in Norwegian air samples